



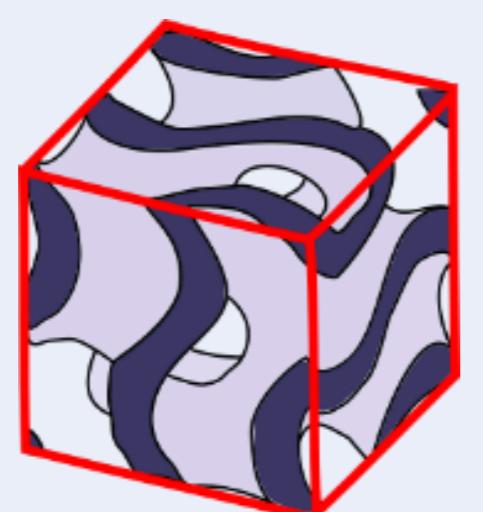
# $\text{SO}_3\text{H}$ -functionalized Periodic Mesoporous (Organo)Silica for catalytic applications

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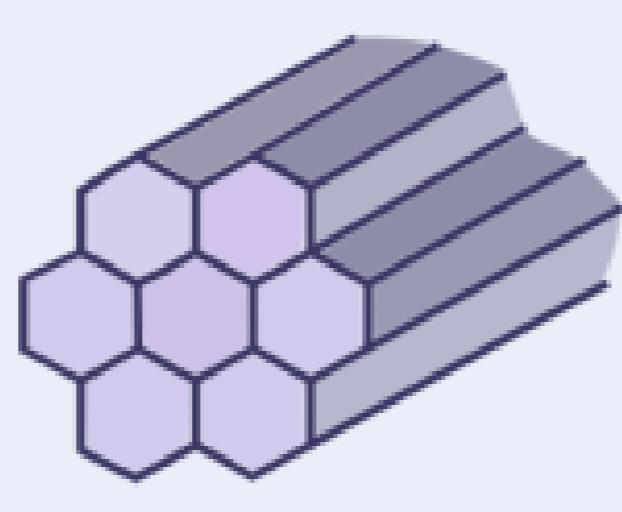
## Introduction I- Mesoporous (Organo)Silica

Mesoporous Silica consists of amorphous condensed  $\text{SiO}_2$ . These materials were synthesized in template assisted sol-gel reactions. After removing the template molecules, ordered pore systems and high specific surface areas up to  $1000 \text{ m}^2\text{g}^{-1}$  were achieved. The most prominent representatives are the so-called MCM-41, SBA-15 and KIT-6.<sup>[1]</sup>

- Possible pore structures of mesoporous silica materials:

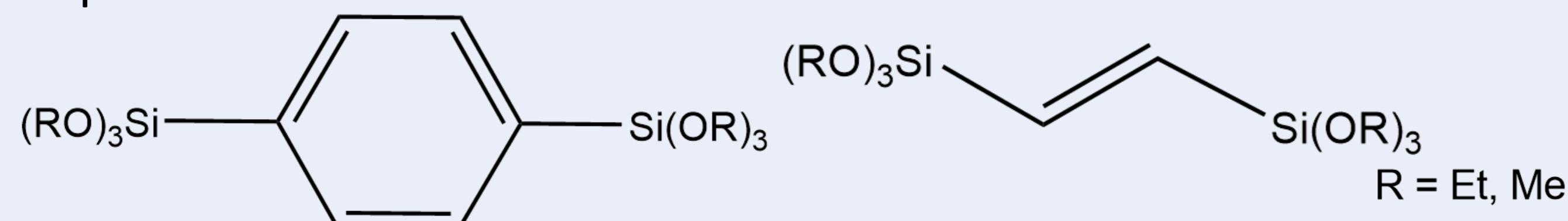


3D cubic,  $Ia\bar{3}d$



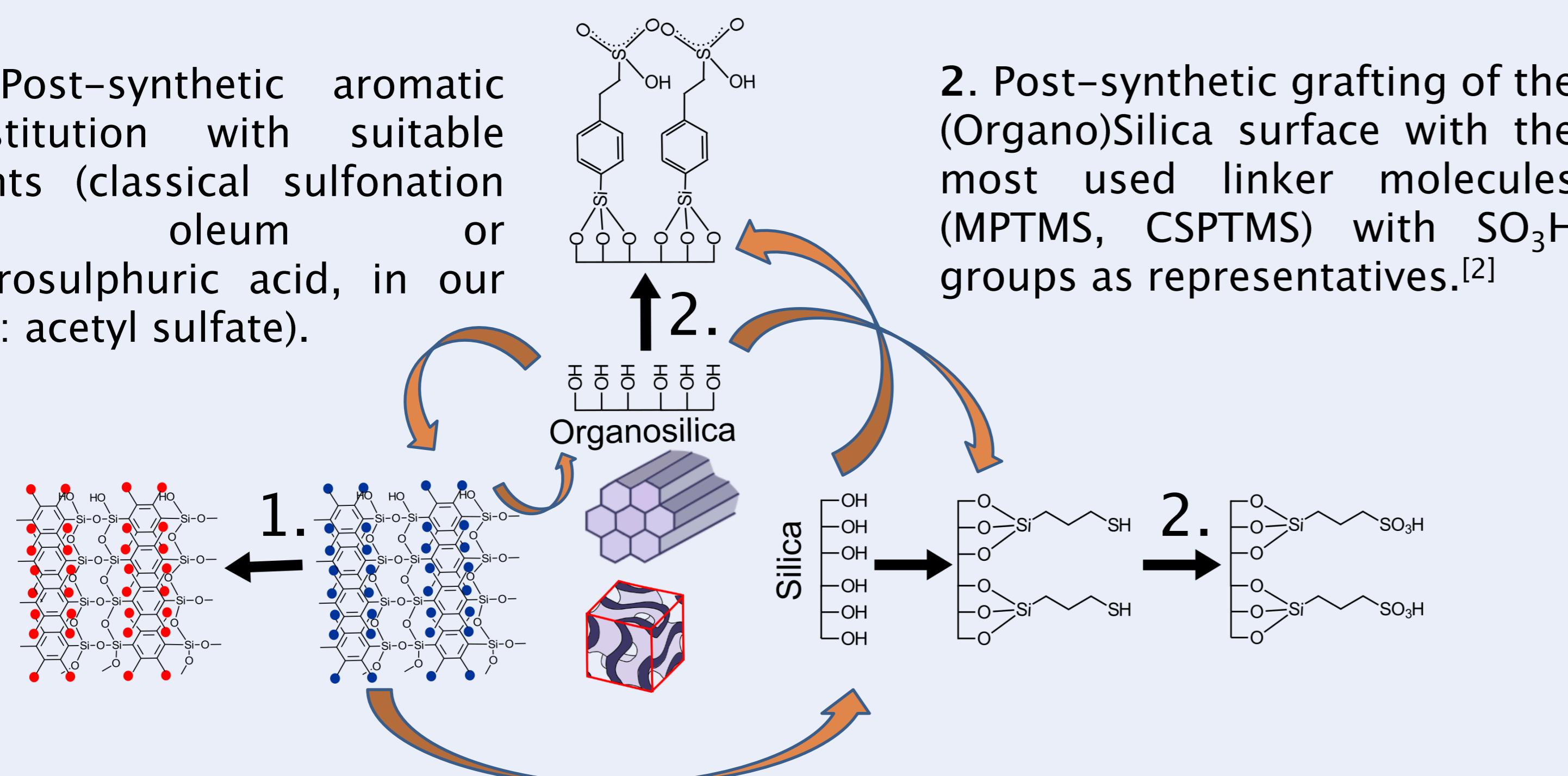
2D hexagonal,  $p6$

- PMO (periodic mesoporous organosilica): periodic arrangement of organic groups in the pore wall due to bisilylated organic precursor molecules



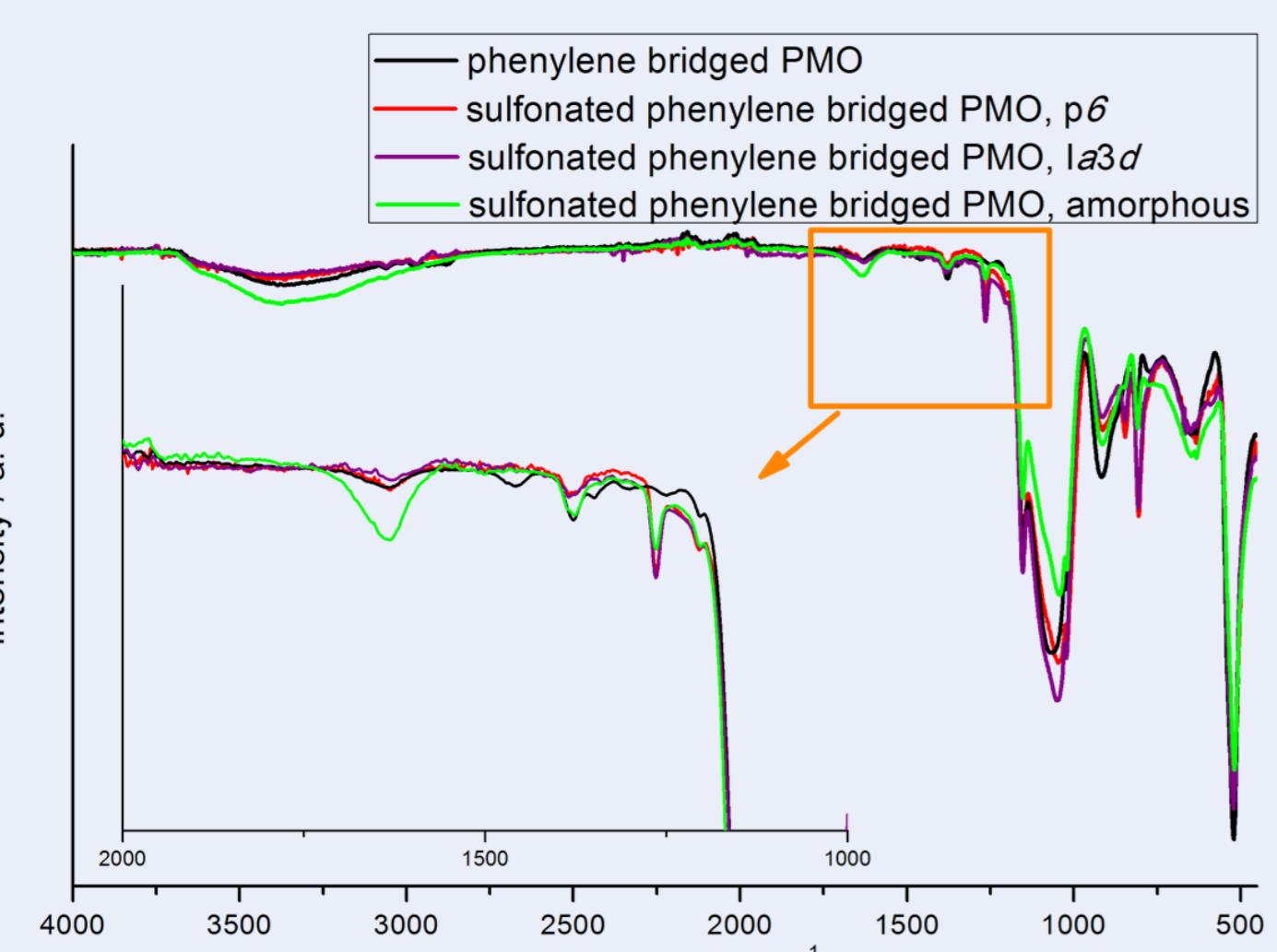
## Sulfonation of (Organo)Silica

- Post-synthetic aromatic substitution with suitable agents (classical sulfonation with oleum or chlorosulphuric acid, in our case: acetyl sulfate).

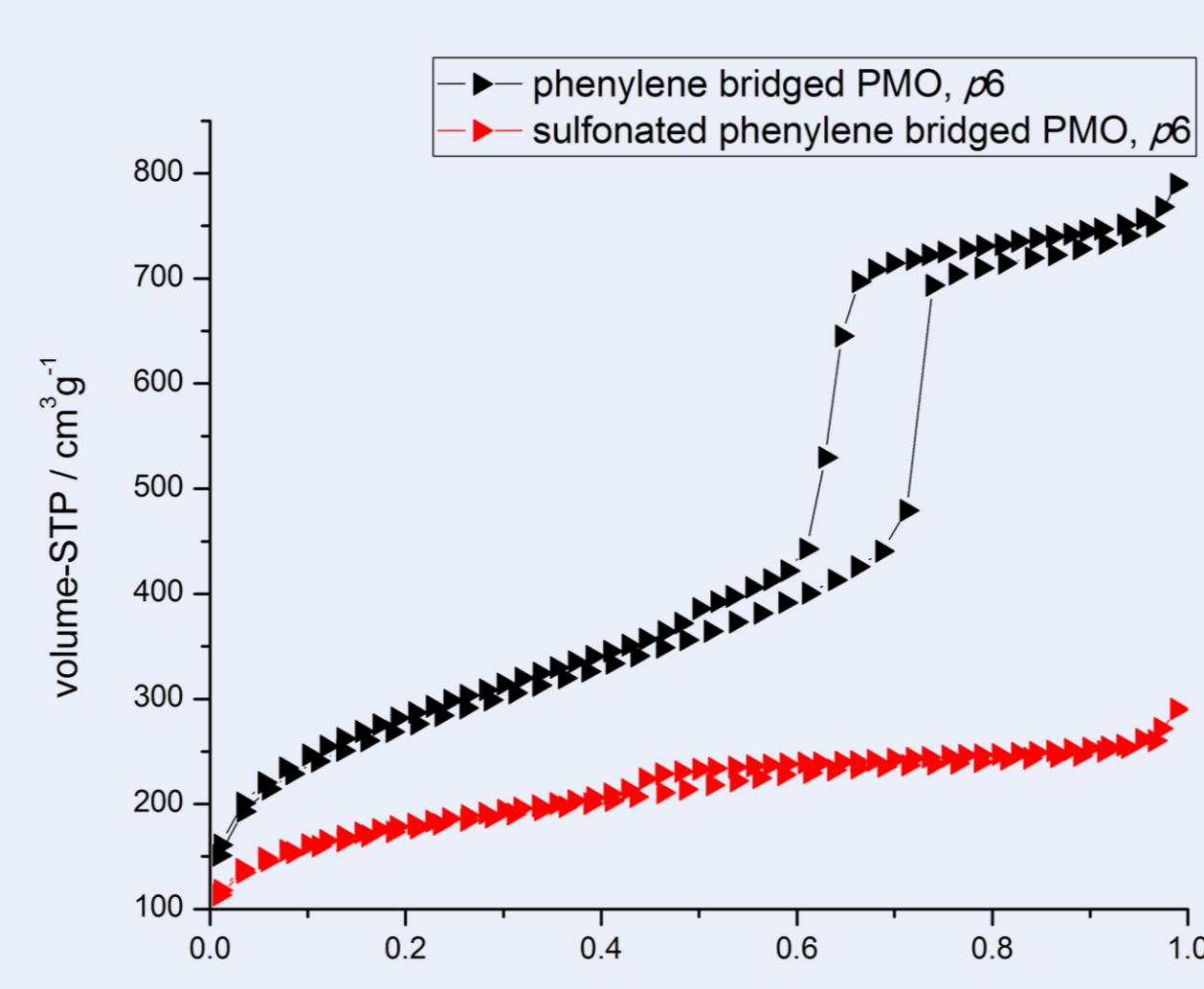


Different options to functionalize the pore walls/ surface of periodic mesoporous (Organo)Silica, either sulfonation with sulphuric acid/oleum (left) or grafting with MPTMS (3-mercaptopropyl trimethoxysilane) followed by thiol group oxidation with hydrogen peroxide. or grafting with 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane (CSPTMS) followed by hydrolysis.

## Sulfonation with acetyl sulfate

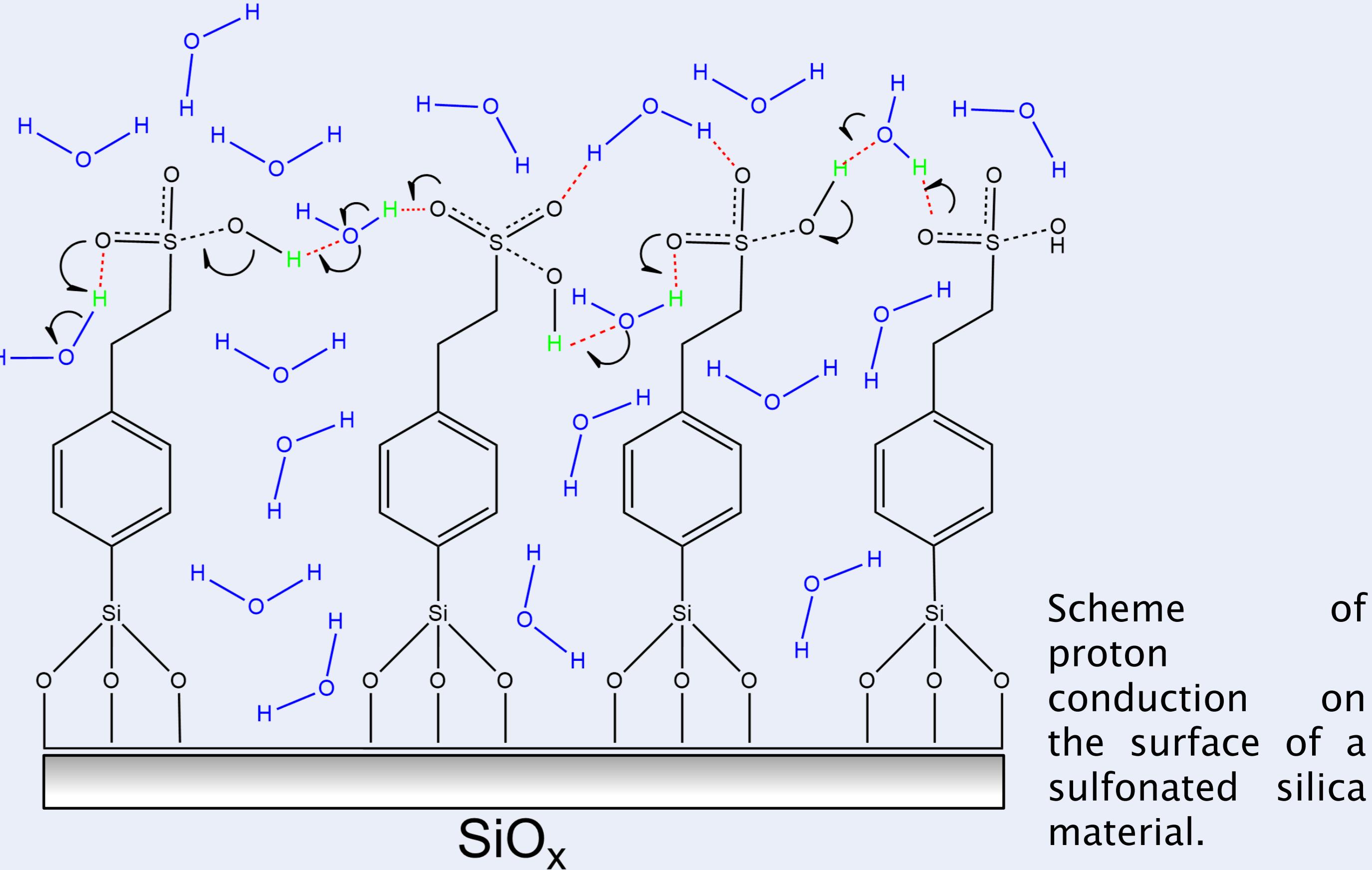


ATR-IR spectra of the sulfonated samples with different pore structures compared to the pure phenylene bridged PMO (black). Additional signal at  $1268 \text{ cm}^{-1} = v_{as}(\text{S}-\text{O})$ <sup>[3]</sup>



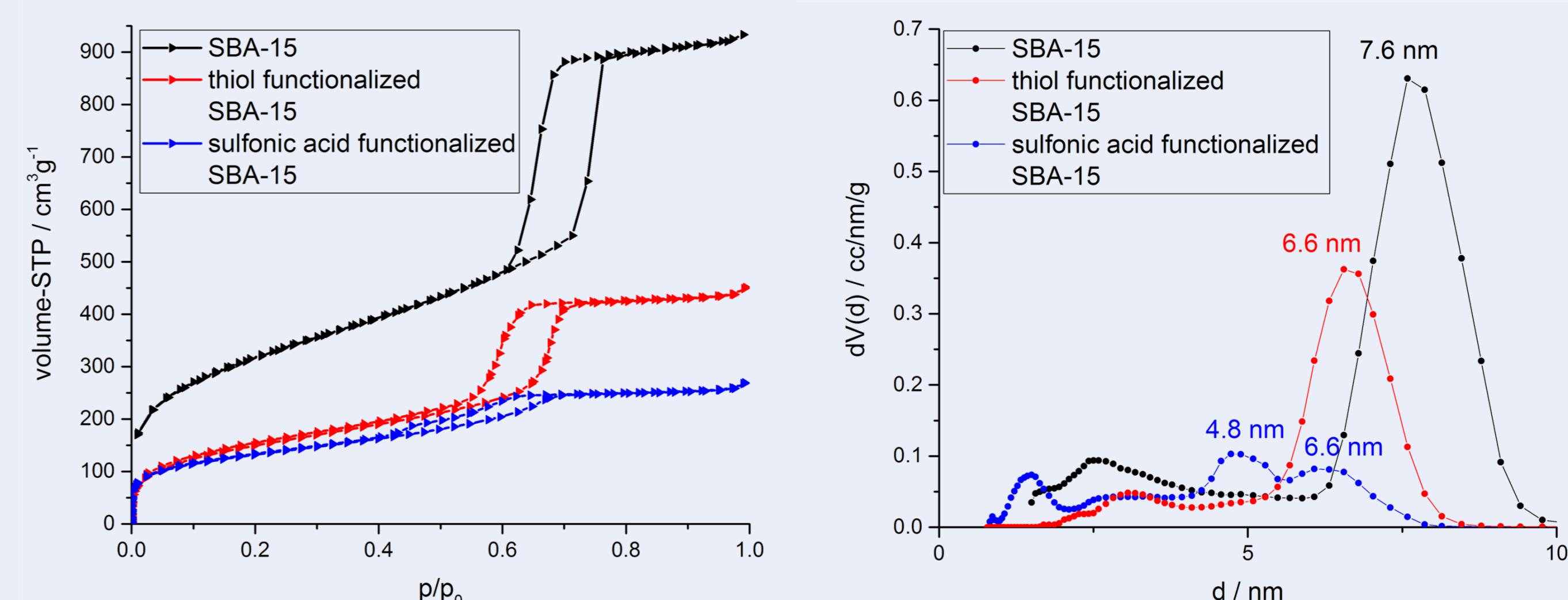
Nitrogen physisorption isotherms of the sulfonated phenylene bridged PMO samples before (black, specific surface area:  $916 \text{ m}^2\text{g}^{-1}$ ) and after the reaction with acetyl sulfate (red, specific surface area:  $560 \text{ m}^2\text{g}^{-1}$ ).

Highly sulfonated mesoporous Silica or Organosilica materials are good proton conductors. This characteristic behavior leads to a wide range of applications. So, these materials are used as functional component in fuel cells or in catalytic processes. The proton conduction of the sulfonated material is water mediated.



## Introduction II- Sulfonated mesoporous Silica

## Sulfonation via grafting with MPTMS



Left: Nitrogen physisorption isotherms of SBA-15 (black, specific surface area:  $1092 \text{ m}^2\text{g}^{-1}$ ), thiol functionalized sample (red, specific surface area:  $544 \text{ m}^2\text{g}^{-1}$ ) and  $\text{H}_2\text{O}_2$  treated,  $\text{SO}_3\text{H}$  functionalized sample (blue, specific surface area:  $457 \text{ m}^2\text{g}^{-1}$ ). Right: Pore size distribution of the functionalized samples via NL-DFT analysis.

After grafting of the MPTMS linker on the silica surface, the specific surface area and pore size decrease. This trend carries on through the oxidation of anchored thiol groups and could be explained with the incorporation of organic units (first functionalization step) and the generation of more sterically demanding sulfonic acid groups compared to thiol groups (second functionalization step).

## Conclusion

The post-synthetic functionalization of mesoporous periodic (Organo)Silica is successfully realized by using different synthetic approaches. The changes of the surface area and the pore size distribution could be monitored by nitrogen physisorption.

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